

THE ROLE OF THERMAL HYDROGEN-TRANSFER PROCESSES IN CATALYTIC COAL LIQUEFACTION

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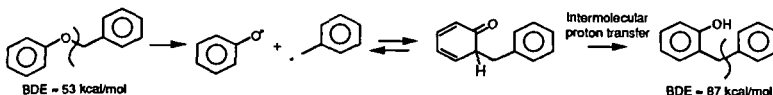
INTRODUCTION

The complexity of coals and their liquefaction products unavoidably means that no "model compound" system can be found that even remotely approaches the real coal in behavior, without also approaching it in intractability of chemical analysis. Notwithstanding these limitations, much has been learned by detailed examination of coal liquefaction phenomenology in light of the behavior of "model" or surrogate structures under liquefaction conditions. Recently we have reviewed¹ some of our own research and other related work that highlights some of what has been learned following this approach. That review summarizes some of the limitations of the formerly accepted weak-bond scission view of donor-solvent coal liquefaction, along with the improved interpretation that emerges when the role of solvent-mediated H-transfer in *actively* promoting bond scission is considered. In addition, the preceding papers in this symposium have highlighted various hydrogen-transfer mechanisms and some key features (and questions) that have evolved during the development of direct coal liquefaction processes.

In this paper, we attempt to build on the background of model compound studies and process development results. We begin by emphasizing two points that have sometimes been lost in discussions of radical reaction mechanisms of hydrocarbon structures. First, high-temperature reactions of coals are not necessarily limited to processes that are purely free-radical: the polar functional groups on coals make it very likely in fact that reactions involving charge separation (i.e., "ionic" reactions) can play some key roles in high temperature coal conversion processes. Second, we assert "thermal" and "catalytic" reactions should *not* be considered as two separate realms of the universe, but as classes of reactions that are *both* important in virtually all catalytic liquefaction processes. Bearing these two points in mind, we then briefly examine some data from the recent literature in an attempt to gain new insight about how cleavage intermediates on iron-based catalyst surfaces may relate to those present in the bulk donor solvent.

IONIC REACTIONS IN BOND-FORMATION AND BOND-CLEAVAGE

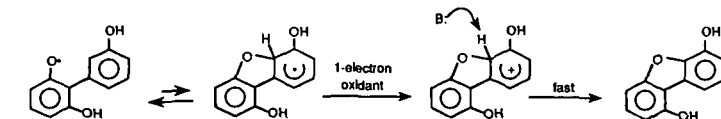
Potential Role of Charged Species and Proton Transfer in Retrograde Reactions. Contrary to the common perception, simple radical recombination reactions are not good candidates for the retrograde processes that plague coal liquefaction, because radical recombination will involve the most stabilized radicals, to generate only the weakest bonds. However, a major exception to this generalization is the case of phenoxy- or other aryloxy radicals. In this case we have suggested¹ that successful retrogression is possible because the highly unstable intermediates generated by ring-recombination of aryloxy radicals are able to rapidly tautomerize through facile intermolecular proton-transfer reactions,² thus locking the original unstable recombination into place. This suggestion is illustrated in Scheme 1 with benzylphenyl ether, and its validity is supported by the reports in the literature³ that the presence of scavengers can decrease, but not easily eliminate, the formation of benzylphenol.



Scheme 1. Retrograde Reaction via Phenoxy Radical Recombination and Rapid Tautomerization.

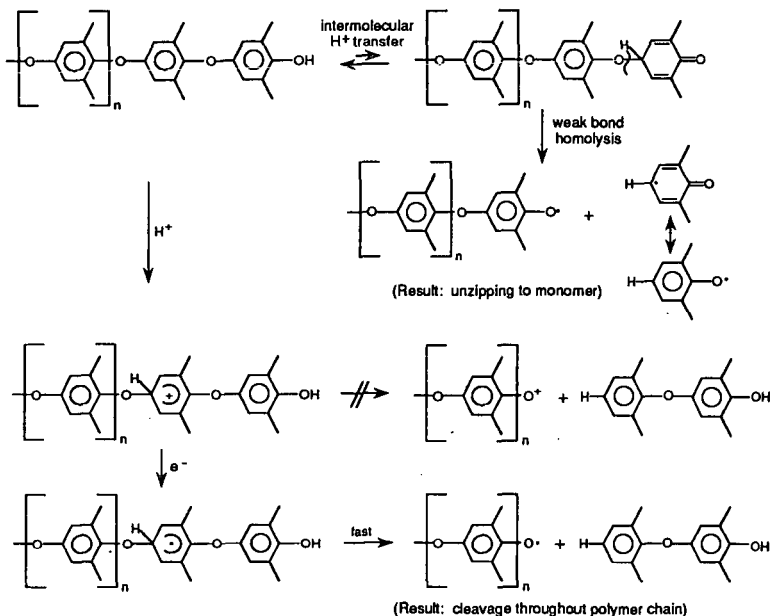
This reaction is one example of interplay between radical and ionic reactions, a phenomenon that may be commonly important in the retrograde processes of oxygen-containing coal structures.

Retrograde Reaction Facilitated by Electron- and Proton- Transfer. The presence of one or more phenolic groups can also promote retrograde reactions that begin with radical addition to an aromatic system. Here removal of the ipso hydrogen is likely enabled not by the relatively high acidity of a keto structure such as in Scheme 1 above, but by the fact that ortho- or para -OH groups on the ipso radical may facilitate its oxidation to the corresponding cation. The cation is very acidic, and can lose a proton extremely rapidly, as suggested⁴ for the products observed in the retrograde reactions of dihydroxyarenes and illustrated in Scheme 2.



Scheme 2. Suggested Completion of Retrograde Reaction by One-Electron Oxidation and Proton Loss.

Bond Cleavage Promoted by Electron- and Proton Transfer. Ten years ago, Solomon and Squire showed⁵ that pyrolysis of poly(2,6-)xlenol in the inlet of a field ionization mass spectrometer results in a rapid, apparently autocatalytic process at about 380°C, yielding a series of oligomers consisting primarily of monomer through hexamer. The carbon-oxygen bond strength in this polymer is about 77 kcal/mol,⁶ far too high to react by simple homolysis at a substantial rate at 400°C. The decomposition of the polymer appears to be predominantly, *but not exclusively*, an unzipping process, since the monomer is in moderate excess over higher oligomers until the final stages of the decomposition process. The reaction is autocatalytic, accelerating as the phenolic products accumulate. Since the reaction proceeds even in the absence of a donor solvent, generation of the main products (which is a reduction process) must be fed by hydrogen from some minor product(s), presumably non-volatile charry material. These factors lead us to suggest the dual-pathway mechanism shown in Scheme 3.



Scheme 3. Suggested Cleavage of Polyxlenol via Proton- and Electron Transfer.

The unzipping process by which the terminal units cleave off to form xlenol is almost certainly the reverse of the phenoxyphenol cleavage we reported some years ago, i.e., the reverse of the retrograde reaction shown in Scheme 1 above. However, reaction via the keto tautomer is not the only significant bond cleavage process, since the homolysis of the much weaker⁷ (ca. 40 kcal/mol) cyclohexadienone-oxygen bond would be about 10^7 times faster (on a per-molecule of original enol starting-material basis) than reaction of the original aryl-oxygen bonds in the polymer. If we consider reaction of polymeric structures of $n = 100$, we should still see cleavage of the end units dominating by a factor of about 10^5 . In fact, for most of the reaction, the monomer dominates over the small oligomers in the product mixtures by factors of only two to three. The degree of accelerated bond cleavage observed here for even the internal aryl-oxygen bonds is far greater than that which has been observed for simple H-atom transfer to diaryl ether from a good donor solvent.⁸ Clearly either this reaction mixture is an unusually good source of free H-atoms, which are reactive enough to readily cleave even simple diphenyl ether structures, or there is something about a phenyl ring with ether linkages in both the 1- and the 4- positions that make it quite susceptible to other cleavage pathways.

We suggest the additional bond cleavage pathway to be considered for internal aryl-O linkages in the polymer chain is the proton-transfer, electron-transfer process also shown in Scheme 3. The rationale here is that oxygen substitution on an aromatic ring system facilitates protonation at certain positions, and electron transfer to the protonated segment results in a net H-transfer, bringing about rapid bond cleavage. Protonation at a carbon bearing an oxygen would itself not readily result in cleavage of the C-O bond, since that would involve elimination of a disfavored aryloxy cation. However, electron transfer following the proton transfer would give the ipso-substituted radical, for which β -scission should then be very facile. In the polymer, there are two oxygens connected to each ring. While one of them deactivates protonation at the ipso position, the other, which is para to that position, promotes it. The para oxygen would also promote simple H-atom transfer, but such H-atom transfer from a good donor solvent to substituted naphthalenes and naphthols is known to be accelerated by factors of only about ten,⁴ whereas here oxygen substitution has accelerated cleavage by many orders of magnitude (as compared to diphenyl ether itself).

It is of course speculative to suggest electron transfer without an identified eT agent, but we are not concerned here with electron transfer near room temperature, but at much higher temperatures, and to a positively charged species. The proton transfer that precedes electron transfer could in fact be facilitated by the high acidity of the very class of keto-form retrograde intermediates shown in the examples given in Scheme 1 above. The net result of the proton-transfer, electron-transfer sequence shown in Scheme 3 is an H-atom transfer. The indirect sequence would of course have significance only if it serves to supplant a kinetically hindered direct H-atom transfer, such as radical hydrogen-transfer (RHT) process, that could otherwise not account for the observed cleavage rates.

To summarize the situation for cleavage of the polyxylenol, two cleavage pathways evidently become operative as coal liquefaction temperatures are approached. One, which cleaves off terminal units that have free phenolic groups, almost certainly occurs through ionic tautomerization to a weakly bonded keto form that undergoes rapid homolysis. The second cleaves O-aryl bonds to internal units that have no free -OH groups. The latter process could involve free H-atoms, but more likely we suggest, involves a proton-transfer, electron-transfer process.

The examples shown in Schemes 1 through 3 demonstrate that heteroatom linkages and functional groups are quite likely to bring ionic reactions into play, often in combination with free radical reactions. In the discussion of iron sulfide catalysis that follows, we take as a starting point the corollary expectation that reactions promoted by iron-oxygen-sulfur surfaces might well involve, even for substrates containing no heteroatoms, the formation of ionic or charge-separated species.

THE ROLE OF THERMAL REACTIONS IN CATALYTIC CONVERSION

It is sometimes said that "thermal" reactions, i.e., donor-solvent-coal interactions, become irrelevant as processes evolve towards more effective use of catalysts. This view is first, clearly not correct, and second, belies the potential value of an understanding of thermal process as a basis for addressing the nature of those processes that are clearly catalytic.

A prime example of thermal reactions playing a key role in a "catalytic" process comes from the field of catalytic resid upgrading (including coal-oil coprocessing). Here, it is well recognized⁹ that the factor having the largest impact on distillate conversion is temperature, and that the distillate generation processes are primarily thermal, rather than catalytic. Thus, even though the feedstock in this case is (at process temperatures) a liquid, and has nominal access to catalyst surfaces, most of the reactions that make distillate actually occur in the bulk reaction medium, remote (in molecular terms) from the catalyst surfaces. Thermal distillate formation is in overall terms essentially a disproportionation process, presumably proceeding to a large degree through Rice-Herzfeld H-abstraction— β -scission chemistry. The distillate materials are derived mainly from the aliphatic portions of the resid molecules, which as they fragment to an alkane-alkene mixture, act as a hydrogen "sponge" and place a severe hydrogen demand on the portions of the resid molecules that are already hydrogen poor. In the absence of more readily available sources of hydrogen, this demand is satisfied by utilizing hydrogen made available from the aromatic centers of the resid molecules, thus driving those PAH towards coke.

Since the distillate formation is largely thermal, it follows that the coke formation that is driven by it is probably also thermal, occurring remote from the catalyst surface. Although the key role of the catalyst is to limit coke formation, what occurs remote from the catalyst surface can only be impacted *indirectly* by the catalyst, that is by "thermal" reactions between the reaction medium and the coke precursors. Thus the essence of catalytic resid upgrading can be summarized by saying it is relatively easy to derive a large fraction of the potential distillate by simply raising the temperature; the key to a more efficient process essentially involves finding the most effective way to supply hydrogen via H₂, catalyst, and reaction medium, thus limiting formation of coke. In other words, efficient, high space-velocity resid conversion requires optimization of the complementary operation of catalytic *and* thermal reactions. Similar arguments can be made for some stages of coal liquefaction.

CLEAVAGE INTERMEDIATES ON IRON- AND IRON SULFIDE SURFACES.

Another sense in which coal-solvent, or "thermal" reactions are relevant to catalytic coal liquefaction lies in current attempts to learn more about the species on iron sulfide catalyst surfaces. These surfaces are now known¹⁰ to promote coal liquefaction and dealkylation of substituted aromatics via intermediates that involve transfer, in some manner, of only a single hydrogen. How might the surface-bound species be similar to (or different from) the intermediates involved in pure solution-phase hydrogenolysis? Are these surface species likely to be free-radical, or is there enough ionic and/or semiconductor character in the critical crystal surfaces or edges to facilitate the formation of charged species?

Several years ago, Wei et al.¹⁰, and more recently, Davis and coworkers,¹¹ and Linehan, et. al.,¹² have used model compounds to study the hydrogen exchange and/or C-C bond cleavage promoted by Fe or FeS surfaces. Their results all provide strong evidence for bond cleavage following transfer of a single hydrogen. The data of Wei et al. indicate that even at 300°C and in the presence of 1450 psi H₂, reaction of 1,1'-dinaphthylmethane is almost exclusively to produce naphthalene and 1-methylnaphthalene, with very little di- or tetra-hydronaphthalene derivatives. These

researchers consider that the intermediate in the cleavage reaction is a surface-bound ipso radical,¹⁰ generated by H-atom transfer to produce intermediates exactly analogous to those involved in solvent-mediated hydrogenolysis. However, the examples discussed above, where the presence of only a few heteroatoms in the coal structure bring ionic reactions into play, should make us alert to the possibility that the surface of an ionic solid may also be promoting reactions that involve electron transfer or charged intermediates.

The nature of the intermediates on various iron surfaces are of particular interest for two very important reasons. First, although cleavage is facile at 300°C for displacement of resonance stabilized radicals¹⁰ (or perhaps cations), displacement of unstabilized radicals appears not to occur even at 400°C.¹² Clearly transfer of a single hydrogen to bring about cleavage of very strong methylene bridges between two aromatic clusters is rapid, whereas displacement of bridges of two or more atoms, where the departing fragment is not resonance stabilized, essentially does not occur on these catalysts. Thus, these surfaces evidently will not cleave diarylethane linkages, but these are in any case weak bonds that will homolyze readily during liquefaction. These surfaces will also not serve to cleave bridges of three or more atoms, but such linkages are susceptible to cleavage via H-abstraction— β -scission. The catalysis will also not cause displacement of simple alkyl groups. Thus, it is clear that such catalysts have the potential to use hydrogen to cleave those linkages it may be most important to cleave, leaving the more labile linkages of two or more atoms to less "expensive" routes (or to occur at a more convenient time), and leaving totally untouched the simple alkyl groups whose displacement would only result in hydrogen consumption and the unwanted formation of methane or other light hydrocarbon gases.

The second reason why these intermediates are of practical interest derives from the fact that the hydrogen needed for the cleavage does not have to come, at least during the coal dissolution step, from high pressure hydrogen. Linehan et al. report¹² using 9,10-dihydrophenanthrene, rather than H₂ gas, as the source of surface hydrogen for model compound studies testing their dispersed iron catalysts. This result is very interesting, because researchers have from time to time explored the possibility of catalytic use of donor hydrogen, sometimes called "transfer hydrogenation." However, what has most often been found is that under conditions with no hydrogen overpressure, typical coal liquefaction catalysts, which of course are usually good hydrogenation catalysts, serve simply as an open valve for rapid dehydrogenation of the donor solvent, while providing very little catalytic aid to the liquefaction itself. Clearly what is needed is a catalyst that allows relatively facile H-transfer from a hydroaromatic to the catalyst surface, but does not allow facile recombination to H₂ and dissociation. In the simplest terms, this would merely require a catalyst or conditions under which the dissociatively adsorbed hydrogen has sufficiently low coverage (and/or low mobility) to limit recombination, but enough coverage to be active in causing single H-atom transfer to positions on aromatic clusters bearing linkages. Since the requirements for low coverage and high activity tend to be conflicting, a balance providing real-world catalytic utility may be difficult to find. Thus it is likely that an effort to substantially accelerate selective catalytic cleavage under conditions where there is no hydrogen overpressure will need to be aided by a better picture of the critical surface-bound species and their reactivity.

Examination of the data of Davis and coworkers¹¹ reveals an observation parallel to the exclusive displacement of resonance-stabilized groups, namely that isotopic exchange of aromatic hydrogens (e.g., on 1-methylnaphthalene), occurs without loss of a methyl fragment. However, this is not what would generally be expected were the surface intermediate an ipso-radical species. As shown in Table 1, the estimated rates of either unimolecular H-atom elimination or bimolecular removal of H-atoms via interaction with solution-phase species are substantially lower than estimated rates of methyl radical elimination (assuming that the thermodynamics of H-atom loss are essentially the same as those for solution-phase ipso-radical species). The differences would be even greater for elimination of ethyl radicals and other non-benzylic fragments.

Ades et al. have suggested¹³ that the iron-sulfide-catalyzed cleavage of the model compound bibenzyl-naphthylmethane involves one-electron oxidation to the radical cation, which then cleaves directly (preferentially giving a naphthyl- and a bibenzylmethyl fragment). However, Penn and Wang¹⁴ have shown that generation of bona fide radical cations, either in solution or in the gas phase, leads preferentially to cleavage of the weakest bond in the original molecule (in this case the bibenzyl linkage) or secondarily to cleavage that gives the most stabilized benzylic fragment (in this case a naphthylmethyl fragment). This contrasts with the observed FeS-catalyzed cleavage, which gives preferential cleavage *between* the methylene linkage and the naphthalene ring.

Autrey et al., in one of the preceding papers in this symposium,¹⁵ also invoke one-electron oxidation, but not direct cleavage of the radical cation. They suggest the inability of the cleavage intermediate to eliminate a simple alkyl fragment may reflect that fact that it actually is a cationic species resulting from electron transfer to the surface, followed by H-atom transfer to the substrate to generate the ipso-cation. Such a species might well exhibit the high selectivity observed for elimination of a benzylic fragment, as compared to a methyl fragment. However, this would be tantamount to an acid-cracking process, for which molybdenum and iron sulfide surfaces are not generally known. Furthermore, a mechanism involving elimination of benzylic cations (from either cation or radical-cation intermediates) would have to account for the absence of transalkylation products by invoking what amounts to a hydride transfer to the benzylic cation before it departs the surface. Thus it appears to us that neither direct cleavage of a radical cation nor formation and cleavage of an acid cracking intermediate offer very satisfactory explanations of the observed bond cleavage.

A partially satisfactory rationalization can be achieved by noting that application of the estimated cleavage rates (Table 1) to surface species requires qualification. The zeroth-order assumption of little change in the thermodynamics of the surface-bound species, relative to the same species in solution, is clearly an oversimplification. Preferential adsorption on the surface of course means stabilization, relative to the bulk solution-phase species. This stabilization will make more difficult the unimolecular elimination of a methyl radical, which will be less strongly bound on the surface than the larger and more polarizable ipso-intermediate. On the other hand, the heat of adsorption of H-atoms on the catalyst surface will very likely be more than that for the ipso intermediate, thus facilitating exchange of the H-atom back to the surface. Thus, by considering, at least in qualitative terms, the relative impacts of surface adsorption on the various species, we can achieve a gross rationalization of the observed fragmentation behavior on iron catalyst surfaces, as compared to that which has already been quantified in the gas phase and/or bulk solution.

Additional support for a surface-bound radical intermediate may lie in the details of the isotopic exchange results briefly described above. Dabbagh et al. report¹¹ not only the total extent of exchange, but also the fraction of total deuterium found at positions 2 through 8 on the 1-methylnaphthalene recovered from the high-temperature exchange and also from a lower temperature (100°C) acid-catalyzed exchange. The deuterium distributions, as shown in Table 2, are very similar in the two cases, *except* for the deuterium content at the position ortho- to the 1-methyl group.

The high temperature, surface-promoted exchange results in only ~9% of the deuterium being located at the 2-position, very similar to the 3-, 6-, and 7- positions, which are the least reactive in the molecule. In contrast, under acid-catalyzed exchange conditions, the 2-position has 30% of the deuterium, almost as much as the most reactive (4-) position. We tentatively conclude that the rapid exchange at the inherently unreactive 2-position under acidic conditions reflects marked stabilization by methyl of the partial positive charge at the 1-position that results from proton attack. In contrast, the minimal enhancement (by 1-methyl substitution) of iron-catalyzed exchange at the 2-position suggests that exchange there occurs via H-atom transfer, since the benefits of creating a tertiary radical center are *much* less than the benefits of creating a tertiary carbocation. This difference is illustrated by the relative enthalpy costs for generating secondary and tertiary cations and radicals ($\Delta\Delta H^\circ_{298}[\text{cation-parent alkane (g)}]$ is 16 kcal/mol greater for generation of the isopropyl cation than for generation of the t-butyl cation [from the respective alkanes], whereas the difference is only 2-3 kcal/mol for generation of the secondary and tertiary radicals¹⁰).

Although the above rationalization of observed cleavage selectivity and H-exchange patterns may remove any compelling need to invoke the generation and decomposition of positively charged hydrocarbon species on the iron surface, we believe the possibility of ionic intermediates should still be kept in mind. It is imprudent to simply assume that decomposition that is aided by adsorption on a surface that is even modestly ionic, and/or has some semiconductor character, does not involve either electron transfer or the formation of charged species. To the extent that the catalytically active surfaces (or edges) are not pure sulfides, but are some class of much more ionic mixed oxysulfides, or to the extent that iron vacancies (as often invoked for pyrrhotite) are present to provide the surface with electron donor/acceptor properties, the possibility of charged intermediates needs to be considered. Moreover, given the inability, via prior- or post- analysis of the inorganic phase, to make definitive statements about the nature of the active catalyst under the *actual reaction conditions*, more systematic use of model compound variations to probe the nature of these catalysts is clearly in order. For instance, the possibility of reaction via cationic intermediates, such as that argued against above, could be further tested by comparing the catalytic decomposition of diarylmethanes to their diaryl ether analogs. Decomposition to give aryloxy cations should be distinctly less favored than decomposition to give arylmethyl cations, whereas decomposition to give aryloxy radicals would if anything be more favored than in the hydrocarbon analog.

There is also a fourth possibility that needs to be considered for these catalytic bond cleavages, namely that *net* H-atom attack might result from 1-electron reduction, followed by proton transfer to the radical ion. Although one-electron reduction is not such an obvious candidate with an iron-deficient surface like pyrrhotite that should show better acceptor, rather than donor, properties,¹³ the exact surface (or edge) properties of a nominal pyrrhotite catalyst under reaction conditions are hardly well known. Such an electron-transfer, proton-transfer sequence could call into play both the electronic properties of the iron sulfide and the weakly acid character of surface sulfhydryl groups¹⁷ to provide a catalyzed route to net H-atom transfer.

Suffice it to say at this point that (1) some species on the iron-oxygen-sulfur surface is bringing about selective C-C bond cleavage while utilizing hydrogen obtained from a donor solvent, (2) to do this without gross dehydrogenation of the solvent to H₂ could be very valuable, and (3) understanding the relationship between these surface species and the ipso-radical intermediates responsible for hydrogenolysis in the bulk donor solvent could be key to optimizing and exploiting such reactions.

SUMMARY AND CONCLUSIONS

Heteroatom functional groups, namely phenolic and ether oxygen, very likely play a key role in coal conversion by facilitating rapid transfer of hydrogen as a proton, both to promote bond cleavage and also to allow strong-bond formation. This proton-transfer may sometimes involve uncharged acidic species, such as keto-forms of phenols, which are common recombination intermediates, and sometimes cations that are formed by one-electron oxidation of radicals. The cleavage of certain oxygen-substituted diaryl ether structures, such as polyxylenol, may be promoted by protonation and reductive electron transfer, followed by facile elimination of an aryloxy radical fragment.

Thermal reactions of donor solvent and coal structures are relevant to catalytic processes first in the sense that these two classes of reactions can operate in a very complementary fashion. Two key examples are catalytic hydrotreatment of heavy oil and coal-oil coprocessing. In these two cases, improved use of catalyst allows higher operability temperature limits that make more effective use of thermal distillate generation processes.

Thermal reactions are also relevant to catalytic processes in the sense that the understanding of thermal bond cleavage processes that has been acquired in the last ten years provides a background for learning about the structure of intermediates on catalyst surfaces. Reexamination of data in the recent literature for model compound cleavage on iron sulfide surfaces results in the following observations.

- The observed products are *not* consistent with those generated from cleavage of bona-fide radicals cations, either in the gas phase or in solution.
- The observed bond cleavage, while consistent in itself with that known to occur for acid cracking, does not result in the transalkylation products commonly seen for solution-phase acid-catalyzed dealkylation.
- The H-exchange that occurs at un-substituted positions, which in all likelihood results from the same type of attack as does the ipso-displacement of linkages, shows a pattern consistent with H-atom, rather than H⁺, attack.
- The increased selectivity for displacement of resonance-stabilized (e.g., benzylic) fragments, and the increased ratio of H-loss/methyl-loss, relative to the observed gas-phase or bulk-solution behavior, can be qualitatively rationalized by expected relative adsorption strengths on the catalyst surfaces.
- The data as yet provide no direct evidence about the possibility that *net* H-atom transfer could proceed by I-electron reduction, followed by proton transfer to the radical ion. Such a sequence could be facilitated by both the electronic properties of the iron sulfide and the weakly acid character of surface sulphydryl groups.

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REFERENCES

1. Malhotra, R.; McMillen, D. F. *Energy & Fuels*, **1993**, *7*, 227.
2. Tupitsyn, I. F.; Komarov, V. I. *Reakts. Sposbn. Org. Soedin.*, **1969**, *6*, 616.
3. Poutsma, M. L., "A Review of Thermolysis Studies of Model Compounds Relevant to Processing of Coal," Oak Ridge National Laboratory Report ORNL/TM-10637, **1987**, p. 95.
4. McMillen, D. F.; Chang, S. -J.; Fleming, R. H.; Laine, R. M.; Malhotra, R.; Nigenda, E.; Ogier, W., "Effect of Amine Solvents and Oxygen Functionalities on Coal Liquefaction," Final Report EPRI Research Project 2147-5 **1985**, p. 6-17.
5. Squire, D. R.; Solomon, P. R.; DiTaranto, M. B., "Synthesis and Study of Polymer Models Representative of Coal Structure - Phase II", Final Report, Gas Research Institute, August, **1985**, p. 92-93.
6. McMillen, D. F.; Golden, D. M., "Hydrocarbon Bond Dissociation Energies," *Annu. Rev. Phys. Chem.*, **1982**, *22*, 497.
7. McMillen, D. F.; Ogier, W. C.; Ross, D. S., *J. Org. Chem.* **1981**, *46*, 3322.
8. McMillen, D. F.; Malhotra, R.; Chang, S. -J.; Fleming, R. H.; Ogier, W. C.; Nigenda, S. E. *Fuel* **1987**, *66*, 889.
9. a. Savage, P. E.; Klein, M. T.; Kukes, S. G., *Fuel*, **1988**, *2*, 619.
b. Khorasheh, F.; Rangwala, H. A.; Gray, M. R.; Dalla Lana, I. G., *Energy & Fuels*, **1989**, *3*, 716.
c. Miki, Y.; Yamadaya, S.; Oba, M.; Sugimoto, Y., *J. Catal.* **1983**, *83*, 371.

10. Wei, X.-Y.; Ogata, E.; Futamura, S.; Kamiya, Y. *Fuel Process. Technol.* **1990**, *26*, 135.
11. a. Dabbagh, H. A.; Shi, B.; Davis, B. H.; Hughes, C. G. *Energy & Fuels*, **1994**, *8*, 219.
b. Shi, B.; Guthrie, R. D.; Davis, B. H. *Energy & Fuels*, **1994**, *8*, 1268.
12. a. Linehan, J. C.; Matson, D. W.; Darab, J. G.; Autrey, S. T.; Franz, J. A.; Camaioni, D. M. *Am. Chem. Soc. Div. Fuel Chem. Preprints* **1994**, *39*(3), 720.
b. Matson, D. W.; Linehan, J. C.; Darab, J. G.; Buehler, M. F. *Energy & Fuels*, **1994**, *8*, 10.
13. Ades, H. F.; Companion, A. L. Subbaswamy, K. R. *Energy & Fuels*, **1994**, *8*, 71.
14. Penn, J. H.; Wang, J.-H. *Energy Fuels*, **1994**, *8*, 421.
15. Franz, J. A.; Camaioni, D. M.; Alnajjar, M. S.; Autrey, T.; Linehan, J. C. *Am. Chem. Soc. Div. Fuel Chem. Preprints* **1995**, *40*, XXX.
16. Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1, 1-816.
17. Shan, H.-Y.; Satterfield, C. N. *Ind. Eng. Chem. Proces. Dev.* **1984**, *23*, 20.

Table 1
Estimated Rates of Unimolecular and Bimolecular Loss of Methyl Radical and
H-atoms from 1-Methylnaphthalene Hydroaryl Radical Intermediates

Loss Process	Estimated Rate Constant (s ⁻¹)
Me• Elimination	1 X 10 ⁴
H• Elimination	3 X 10 ³
H-Loss by RD ^a .	<1 X 10 ²
H-Loss by RHT ^b .	≤3 X 10 ³

- a. Pseudo-first-order rate constant for H-loss by radical disproportionation, where [R•]_{tot} is assumed to be dominated by the α-tetralyl radical, and is estimated to be less than 10⁻⁷ M in 90% naphthalene/10% tetralin.
- b. Pseudo-first-order rate constant for H-loss by radical hydrogen-transfer, based on [naphthalene] = ~5M, and on a lower limit for RHT intrinsic activation energy of 17 kcal/mol.

Table 2
Substitution Patterns for Catalysis of Deuterium Exchange by Stainless Steel or
Homogeneous Acids, from Data of Dabbagh et al.

1-Methylnaphthalene Ring Position	% of Total Aromatic Deuterium	
	SS-Catalyzed @ 385°C	Acid-Catalyzed @ 100°C
2	9	30
3	5	11
4	47	35
5	17	11
6,7	5	6
8	17	14